

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
22 August 2002 (22.08.2002)

PCT

(10) International Publication Number
WO 02/064710 A2(51) International Patent Classification⁷: C10M 101/02,
C10G 2/00, 45/58GERMAINE, Gilbert, Robert, Bernard [FR/FR]; Route
Departmentale no. 3, F-76650 Petit Couronne (FR). WED-
LOCK, David, John [GB/GB]; Pool Lane, Ince, Chester,
Cheshire CH2 4NU (GB).

(21) International Application Number: PCT/EP02/01634

(22) International Filing Date: 13 February 2002 (13.02.2002)

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

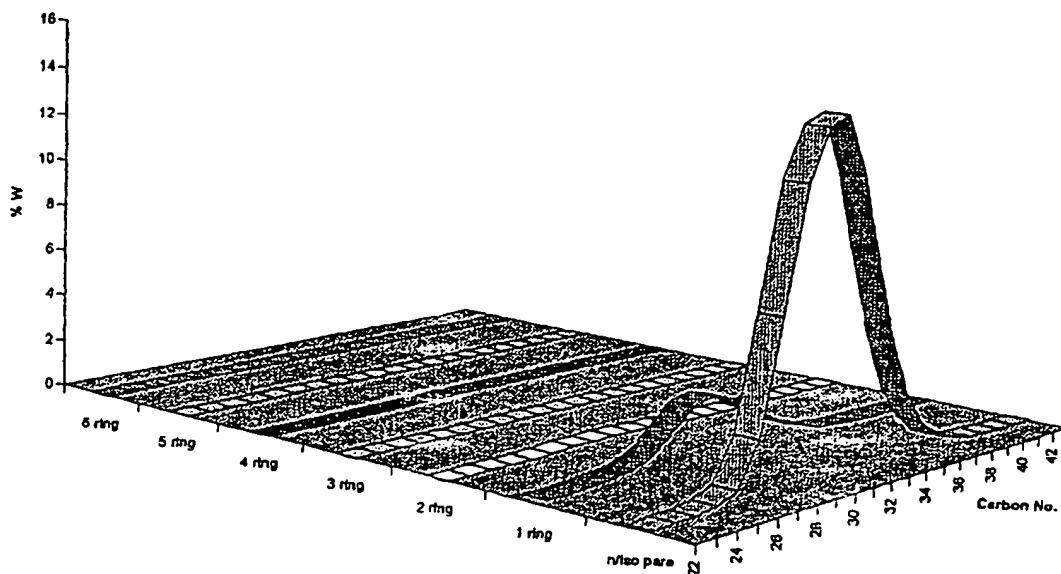
(30) Priority Data:
01301272.9 13 February 2001 (13.02.2001) EP
01400562.3 5 March 2001 (05.03.2001) EP
01402181.0 16 August 2001 (16.08.2001) EP(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).(71) Applicant (for all designated States except US): SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V. [NL/NL]; Carel van Bylandlaan 30, NL-2596 HR
The Hague (NL).

Published:

— without international search report and to be republished
upon receipt of that report

[Continued on next page]

(54) Title: BASE OIL COMPOSITION



WO 02/064710 A2

(57) Abstract: Lubrication base oil composition comprising at least 95 wt % saturates, of which saturates fraction between 19 and 30 wt % are cyclo-paraffins and the remainder being n- and iso-paraffins, said composition having a viscosity index of above 120 and a pour point of below -15 °C.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

BASE OIL COMPOSITION

The invention is directed to a lubricating base oil composition comprising at least 95 wt% saturates, of which saturates fraction between 10 and 40 wt% are cyclo-paraffins and the remainder being n- and iso-paraffins, 5 said composition having a viscosity index of above 120 and a pour point of below -15 °C.

Known from WO-A-0014179, WO-A-0014183, WO-A-0014187 and WO-A-0014188 are lubricant base stock comprising at least 95 wt% of non-cyclic isoparaffins. WO-A-0118156 10 describes a base oil derived from a Fischer-Tropsch product having a naphthenics content of less than 10%. Also the base oils as disclosed in applicant's patent applications EP-A-776959 or EP-A-668342 have been found to comprise less than 10 wt% of cyclo-paraffins. 15 Applicants repeated Example 2 and 3 of EP-A-776959 and base oils were obtained, from a waxy Fischer-Tropsch synthesis product, wherein the base oils consisted of respectively about 96 wt% and 93 wt% of iso- and normal paraffins. Applicants further prepared a base oil having 20 a pour point of -21 °C by catalytic dewaxing a Shell MDS Waxy Raffinate (as obtainable from Shell MDS Malaysia Sdn Bhd) using a catalyst comprising synthetic ferrierite and platinum according to the teaching of EP-A-668342 and found that the content of iso- and normal paraffins was 25 about 94 wt%. Thus these prior art base oils derived from a Fischer-Tropsch synthesis product had at least a cyclo-paraffin content of below 10 wt%. Furthermore the base oils as disclosed by the examples of application WO-A-9920720 will not comprise a high cyclo-paraffin 30 content. This because feedstock and preparation used in said examples is very similar to the feedstock and

preparation to prepare the above prior art samples based on EP-A-776959 and EP-A-668342.

Applicants have now found a lubricating base oil composition having an improved solvency when compared to 5 the disclosed base oils. This is found to be advantageous in for example industrial formulations such as turbine oils and hydraulic oils comprising for the greater part the base oil according to the invention. Furthermore the base oil compositions will cause seals in for example 10 motor engines to swell more than the prior art base oils. This is advantageous because due to said swelling less lubricant loss will be observed in certain applications. Applicants have found that such a base oil is an 15 excellent API Group III base oil having improved solvency properties.

The lubricating base oil composition comprises preferably at least 98 wt% saturates, more preferably at least 99.5 wt% saturates and most preferably at least 99.9 wt%. This saturates fraction in the base oil 20 comprises between 10 and 40 wt% of cyclo-paraffins. Preferably the content of cyclo-paraffins is less than 30 wt% and more preferably less than 20 wt%. Preferably the content of cyclo-paraffins is at least 12 wt% and more preferably at least 15 wt%. The unique and novel 25 base oils are further characterized in that the weight ratio of 1-ring cyclo-paraffins relative to cyclo-paraffins having two or more rings is greater than 3 preferably greater than 5. It was found that this ratio is suitably smaller than 15.

30 The cyclo-paraffin content as described above is measured by the following method. Any other method resulting in the same results may also be used. The base oil sample is first separated into a polar (aromatic) phase and a non-polar (saturates) phase by making use of 35 a high performance liquid chromatography (HPLC) method

IP368/01, wherein as mobile phase pentane is used instead of hexane as the method states. The saturates and aromatic fractions are then analyzed using a Finnigan MAT90 mass spectrometer equipped with a Field desorption/Field Ionisation (FD/FI) interface, wherein FI (a "soft" ionisation technique) is used for the semi-quantitative determination of hydrocarbon types in terms of carbon number and hydrogen deficiency. The type classification of compounds in mass spectrometry is determined by the characteristic ions formed and is normally classified by "z number". This is given by the general formula for all hydrocarbon species: C_nH_{2n+z} . Because the saturates phase is analysed separately from the aromatic phase it is possible to determine the content of the different (cyclo)-paraffins having the same stoichiometry. The results of the mass spectrometer are processed using commercial software (poly 32; available from Sierra Analytics LLC, 3453 Dragoo Park Drive, Modesto, California GA95350 USA) to determine the relative proportions of each hydrocarbon type and the average molecular weight and polydispersity of the saturates and aromatics fractions.

The base oil composition preferably has a content of aromatic hydrocarbon compounds of less than 1 wt%, more preferably less than 0.5 wt% and most preferably less than 0.1 wt%, a sulphur content of less than 20 ppm and a nitrogen content of less than 20 ppm. The pour point of the base oil is preferably less than -30 °C and more preferably lower than -40 °C. The viscosity index is higher than 120. It has been found that the novel base oils typically have a viscosity index of below 140. The kinematic viscosity at 100 °C of the base oil is preferably between 3.5 and 6 cSt and the Noack volatility is between 6 and 14 wt%.

Applicants found that the base oil according to the invention is suitably prepared according to the following process wherein the following steps are performed:

(a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic Fischer-Tropsch product, which product has a weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product of at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms

10 (b) hydrocracking/hydroisomerising the Fischer-Tropsch product,

15 (c) separating the product of step (b) into one or more gas oil fractions, a base oil precursor fraction and a higher boiling fraction,

(d) performing a pour point reducing step to the base oil precursor fraction obtained in step (c), and

20 (e) recovering the lubricating base oil from the effluent of step (d).

Step (a) is preferably performed by making use of a specific catalyst in order to obtain the relatively heavy Fischer-Tropsch product. The Fischer-Tropsch catalyst is suitably a cobalt-containing catalyst as obtainable by

25 (aa) mixing (1) titania or a titania precursor, (2) a liquid, and (3) a cobalt compound, which is at least partially insoluble in the amount of liquid used, to form a mixture; (bb) shaping and drying of the mixture thus obtained; and (cc) calcination of the composition thus obtained.

30 Preferably at least 50 weight percent of the cobalt compound is insoluble in the amount of liquid used, more preferably at least 70 weight percent, and even more preferably at least 80 weight percent, and most

preferably at least 90 weight percent. Preferably the cobalt compound is metallic cobalt powder, cobalt hydroxide or an cobalt oxide, more preferably Co(OH)_2 or Co_3O_4 . Preferably the cobalt compound is used in an amount of up to 60 weight percent of the amount of refractory oxide, more preferably between 10 and 40 wt percent. Preferably the catalyst comprises at least one promoter metal, preferably manganese, vanadium, rhenium, ruthenium, zirconium, titanium or chromium, most preferably manganese. The promoter metal(s) is preferably used in such an amount that the atomic ratio of cobalt and promoter metal is at least 4, more preferably at least 5. Suitably at least one promoter metal compound is present in step (aa). Suitably the cobalt compound is obtained by precipitation, optionally followed by calcination. Preferably the cobalt compound and at least one of the compounds of promoter metal are obtained by co-precipitation, more preferably by co-precipitation at constant pH. Preferably the cobalt compound is precipitated in the presence of at least a part of the titania or the titania precursor, preferably in the presence of all titania or titania precursor. Preferably the mixing in step (aa) is performed by kneading or mulling. The thus obtained mixture is subsequently shaped by pelletising, extrusion, granulating or crushing, preferably by extrusion. Preferably the mixture obtained has a solids content in the range of from 30 to 90% by weight, preferably of from 50 to 80% by weight. Preferably the mixture formed in step (aa) is a slurry and the slurry thus-obtained is shaped and dried by spray-drying. Preferably the slurry obtained has a solids content in the range of from 1 to 30% by weight, more preferably of from 5 to 20% by weight. Preferably the calcination is carried out at a temperature between 400

and 750 °C, more preferably between 500 and 650 °C.

Further details are described in WO-A-9934917.

The process is typically carried out at a temperature in the range from 125 to 350 °C, preferably 175 to 5 275 °C. The pressure is typically in the range from 5 to 150 bar abs., preferably from 5 to 80 bar abs., in particular from 5 to 50 bar abs. Hydrogen (H₂) and carbon monoxide (synthesis gas) is typically fed to the process at a molar ratio in the range from 0.5 to 2.5. The gas 10 hourly space velocity (GHSV) of the synthesis gas in the process of the present invention may vary within wide ranges and is typically in the range from 400 to 10000 Nl/l/h, for example from 400 to 4000 Nl/l/h. The term GHSV is well known in the art, and relates to the 15 volume of synthesis gas in Nl, i.e. litres at STP conditions (0 °C and 1 bar abs), which is contacted in one hour with one litre of catalyst particles, i.e. excluding interparticular void spaces. In the case of a fixed catalyst bed, the GHSV may also be expressed as per 20 litre of catalyst bed, i.e. including interparticular void space. Step (a) can be performed in a slurry reactor or preferably in a fixed bed. Further details are described in WO-A-9934917.

The Fischer-Tropsch product obtained in step (a), 25 optionally after separating some of the lower boiling compounds, for example the compounds having 4 carbon atoms or less and any compounds having a boiling point in that range, is used in step (b). This product has at least 30 wt%, preferably at least 50 wt% and more 30 preferably at least 55 wt%, of compounds having at least 30 carbon atoms. Furthermore the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of the Fischer-Tropsch product is at least 0.2, preferably at least 0.4 35 and more preferably at least 0.55. Preferably the

5 Fischer-Tropsch product comprises a C₂₀⁺ fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at 10 least 0.955. The initial boiling point of the Fischer-Tropsch product may range up to 400 °C, but is preferably below 200 °C.

10 The Fischer-Tropsch product as described in detail above suitably has a content of non-branched compounds of above 80 wt%. In addition to the Fischer-Tropsch product obtained in step (a) also other fractions may be 15 additionally processed in step (b). A possible other fraction may suitably be the higher boiling fraction obtained in step (c) or part of said fraction.

15 The Fischer-Tropsch product will contain no or very little sulphur and nitrogen containing compounds. This is typical for a product derived from a Fischer-Tropsch reaction, which uses synthesis gas containing almost no 20 impurities. Sulphur and nitrogen levels will generally be below the detection limit, which is currently 1 ppm for nitrogen and 5 ppm for sulphur.

25 The Fischer-Tropsch product can optionally be subjected to a mild hydrotreatment step before performing step (b) in order to remove any oxygenates and saturate any olefinic compounds present in the reaction product of the Fischer-Tropsch reaction. Such a hydrotreatment is described in EP-B-668342.

30 The hydrocracking/hydroisomerisation reaction of step (b) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen from those known to one skilled in the art as being suitable for this reaction. Catalysts for use in step (b) typically comprise an acidic functionality and a 35 hydrogenation/dehydrogenation functionality. Preferred acidic functionalities are refractory metal oxide

carriers. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the catalyst for use in the process of this invention are 5 silica, alumina and silica-alumina. A particularly preferred catalyst comprises platinum or platinum/palladium supported on a silica-alumina carrier. If desired, applying a halogen moiety, in particular fluorine, or a phosphorous moiety to the carrier, may 10 enhance the acidity of the catalyst carrier. Examples of suitable hydrocracking/hydroisomerisation processes and suitable catalysts are described in WO-A-0014179, EP-A-532118, EP-B-666894 and the earlier referred to EP-A-776959. The hydrocracking catalyst may also contain 15 a molecular sieve as for example described in US-A-5362378.

Preferred hydrogenation/dehydrogenation functionalities are Group VIII noble metals, for example palladium and more preferably platinum or platinum/palladium alloys. The catalyst may comprise the 20 hydrogenation/dehydrogenation active component in an amount of from 0.005 to 5 parts by weight, preferably from 0.02 to 2 parts by weight, per 100 parts by weight of carrier material. A particularly preferred catalyst 25 for use in the hydroconversion stage comprises platinum in an amount in the range of from 0.05 to 2 parts by weight, more preferably from 0.1 to 1 parts by weight, per 100 parts by weight of carrier material. The catalyst may also comprise a binder to enhance the strength of the 30 catalyst. The binder can be non-acidic. Examples are clays and other binders known to one skilled in the art.

In step (b) the feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. The temperatures typically will be in the range 35 of from 175 to 380 °C, preferably higher than 250 °C and

more preferably from 300 to 370 °C. The pressure will typically be in the range of from 10 to 250 bar and preferably between 20 and 80 bar. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 5 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower than 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 10 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.

The conversion in step (b) as defined as the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C, is at least 20 wt%, preferably at least 25 wt%, but preferably not 15 more than 80 wt%, more preferably not more than 65 wt%. The feed as used above in the definition is the total hydrocarbon feed fed to step (b), thus also any optional recycles, such as the higher boiling fraction as obtained in step (c).

20 In step (c) the product of step (b) is separated into one or more gas oil fractions, a base oil precursor fraction having preferably a T10wt% boiling point of between 200 and 450 °C and a T90wt% boiling point of between 300 and 650 preferably 550 °C and a higher 25 boiling fraction. By performing step (d) on the preferred narrow boiling base oil precursor fraction obtained in step (c) a haze free base oil grade can be obtained having also excellent other quality properties. The separation is preferably performed by means of a first 30 distillation at about atmospheric conditions, preferably at a pressure of between 1.2-2 bara, wherein the gas oil product and lower boiling fractions, such as naphtha and kerosine fractions, are separated from the higher boiling 35 fraction of the product of step (b). The higher boiling fraction, of which suitably at least 95 wt% boils above

350 preferably above 370 °C, is subsequently further separated in a vacuum distillation step wherein a vacuum gas oil fraction, the base oil precursor fraction and the higher boiling fraction are obtained. The vacuum
5 distillation is suitably performed at a pressure of between 0.001 and 0.05 bara.

In step (d) the base oil precursor fraction obtained in step (c) is subjected to a pour point reducing treatment. With a pour point reducing treatment is
10 understood every process wherein the pour point of the base oil is reduced by more than 10 °C, preferably more than 20 °C, more preferably more than 25 °C.

15 Preferably step (d) is performed by means of a catalytic dewaxing process. With such a process it has been found that base oils having a pour point of below -20 °C and even below -40 °C can be prepared when starting from a base oil precursor fraction as obtained in step (c).

20 The catalytic dewaxing process can be performed by any process wherein in the presence of a catalyst and hydrogen the pour point of the base oil precursor fraction is reduced as specified above. Suitable dewaxing catalysts are heterogeneous catalysts comprising a molecular sieve and optionally in combination with a
25 metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size
30 zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48. Another preferred group of molecular sieves are the
35 silica-aluminophosphate (SAPO) materials of which SAPO-11

is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with 5 an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of suitable molecular sieves and dewaxing conditions are for 10 example described in WO-A-9718278, US-A-5053373, US-A-5252527 and US-A-4574043.

The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, silica 15 and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The binder is preferably a porous binder material, for example a refractory oxide of which examples are: alumina, silica-alumina, silica-magnesia, silica- 20 zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a 25 low acidity refractory oxide binder material, which is essentially free of alumina, is used. Examples of these binder materials are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these of which examples are listed above. The most preferred binder is silica.

30 A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is essentially free of alumina as described above, wherein the surface of the aluminosilicate zeolite crystallites 35 has been modified by subjecting the aluminosilicate

zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as 5 described in for example US-A-5157191. Examples of suitable dewaxing catalysts as described above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and dealuminated Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22, as 10 for example described in WO-A-0029511 and EP-B-832171.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, 15 preferably from 40 to 70 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 20 100 to 2,000 litres of hydrogen per litre of oil. By varying the temperature between 315 and 375 °C at between 40-70 bars, in the catalytic dewaxing step it is possible to prepare base oils having different pour point specifications varying from suitably -10 to below -60 °C.

25 After performing a catalytic dewaxing step (d) lower boiling compounds formed during catalytic dewaxing are removed, preferably by means of distillation, optionally in combination with an initial flashing step. The remaining fraction can be further separated into one or 30 more base oil products, wherein at least one base oil product is the base oil composition according to the present invention.

The base oils according to the invention can be 35 suitably used as part of a motor engine lubricant composition comprising also at least one lubricant

additive. Because of its improved solvency as compared to poly-alpha olefins or to the base oils having the lower cyclo-paraffin content as disclosed in the above cited publications it has been found possible to advantageously 5 formulate said lubricants without having to add substantial volumes of (di-)esters which are typically used to increase the solvency of said base oils. Preferably the content of such additional base oil is less than 10 wt% in said formulation.

10 More preferably the lubricant composition comprises the base oil and one or more additives wherein the lubricant composition has a kinematic viscosity at 100 °C of more than 5.6 cSt, a cold cranking simulated dynamic viscosity at -35 °C according to ASTM D 5293 of less than 15 62 centiPoise (cP) and a mini rotary viscosity test value of less than 60000 cP according to ASTM D 4684.

Such lubricant compositions are also referred to as SAE 0W-x compositions. SAE stands for Society of 20 Automotive Engineers in the USA. The "0" number in such a designation is associated with a maximum viscosity requirement at -35 °C for that composition as measured typically by a cold cranking simulator (VdCCS) under high shear. The second number "x" is associated with a kinematic viscosity requirement at 100 °C.

25 The minimum high temperature viscosity requirement at 100 °C is intended to prevent the oil from thinning out too much during engine operation, which can lead to excessive wear and increased oil consumption. The maximum low temperature viscosity requirement, VdCCS, is intended 30 to facilitate engine starting or cranking in cold weather. To ensure pumpability the cold oil should readily flow or slump into the well for the oil pump, otherwise the engine can be damaged due to insufficient lubrication. The mini rotary viscosity (MRV) requirement 35 is intended to ensure a minimum pumpability performance.

The base oil as obtainable by the above processes has a pour point of less than -39 °C and a kinematic viscosity at 100 °C which is suitably between 4 and 8 cSt. The 5 actual kinematic viscosity at 100 °C will depend on the specific 0W-x grade one wishes to prepare. For the 0W-20 and 0W-30 lubricant grades a base oil having a kinematic viscosity at 100 °C of between 3.8 and 5.5 cSt is suitably used. For an 0W-40 grade a base oil having a 10 kinematic viscosity at 100 °C of between 5.5 and 8 cSt is suitably used.

Such a lubricant formulation is preferably used as an 0W-x passenger car motor oil or 0W-x heavy duty diesel engine oil, wherein x is 20, 30 or 40.

The 0W-x lubricant composition comprises one or more 15 additives. Examples of additive types which may form part of the composition are dispersants, detergents, viscosity modifying polymers, extreme pressure/antiwear additives, antioxidants, pour point depressants, emulsifiers, demulsifiers, corrosion inhibitors, rust inhibitors, 20 antistaining additives, friction modifiers. Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pages 477-526.

Suitably the anti-wear additive is a zinc dialkyl 25 dithiophosphate. Suitably the dispersant is an ashless dispersant, for example polybutylene succinimide polyamines or Mannic base type dispersants. Suitably the detergent is an over-based metallic detergent, for example the phosphonate, sulfonate, phenolate or 30 salicylate types as described in the above referred to General Textbook. Suitably the antioxidant is a hindered phenolic or aminic compound, for example alkylated or styrenated diphenylamines or ionol derived hindered phenols. Suitably the viscosity modifier is a viscosity 35 modifying polymer, for example polyisobutylenes, olefin

copolymers, polymethacrylates and polyalkylstyrenes and hydrogenated polyisoprene star polymer (Shellvis).

Examples of suitable antifoaming agents are polydimethylsiloxanes and polyethylene glycol ethers and esters.

5 Another class of lubricant applications are industrial oil formulations, preferably turbine oils and hydraulic oils. Preferred formulations comprise more than 90 wt% of the base oil according to the present invention and between 0.5 and 3 wt% and preferably less than
10 2.5 wt% of an additive. The additives may be additives suited for the above applications, which are well known to one skilled in the art.

The invention shall be illustrated by means of the following non-limiting examples.

15 Example 1
Example 1 illustrates the process to prepare a base oil having a higher cyclo-paraffin content.

A Fischer-Tropsch product was made having boiling curve as in Table 1 by repeating Example VII of
20 WO-A-9934917 using the catalyst as prepared in Example III of the same publication and subsequently removing the C₄ and lower boiling compounds from the effluent of the synthesis reaction. The feed contained about 60 wt% C₃₀₊ product. The ratio C<sub>60+}/C₃₀₊ was about
25 0.55.</sub>

Table 1

| Recovered (wt%) | Temperature (°C) |
|-----------------------|------------------|
| Initial boiling point | 82 |
| 10 | 249 |
| 30 | 424 |
| 50 | 553 |
| 70 | 671 |
| 90 | >750 |

The Fischer-Tropsch product as thus obtained was continuously fed to a hydrocracking step (step (a)). In the hydrocracking step the Fischer-Tropsch product and a recycle stream consisting of the 370 °C⁺ fraction of the effluent of step (a) was contacted with a hydrocracking catalyst of Example 1 of EP-A-532118 at a reactor temperature of 330 °C. The Fischer-Tropsch product WHSV was contacted at 0.8 kg/l.h and the recycle stream was contacted at 0.2 kg/l.h at a total pressure of 35 bar and a hydrogen partial pressure of 33 bar. The recycle gas rate was 2000 Nl/kg of total feed. The conversion of compounds boiling above 370 °C in the total feed which were converted to products boiling below 370 °C was 55 wt%. The product of the hydrocracking step was distilled into one or more fuels fractions boiling in the naphtha, kerosene and gas oil range and a bottom product boiling above 370 °C.

The 370 °C⁺ fraction thus obtained was in turn distilled in a vacuum distillation column, wherein the feed rate to the column was 750 g/h, the pressure at the top was kept at 0.4 mm Hg (0.5 mbar) and the temperature at the top was kept at 240 °C, which is equal to an atmospheric cut off temperature of 515 °C. The top

product had thus a boiling range of between 370 and 515 °C. Further properties were a pour point of +18 °C and a kinematic viscosity at 100 °C of 3.8 cSt. This top product was further used as the base oil precursor fraction in step (c).

5 In the dewaxing step (c) the base oil precursor fraction was contacted with a dealuminated silica bound ZSM-5 catalyst comprising 0.7% by weight Pt and 30 wt% ZSM-5 as described in Example 9 of WO-A-0029511. The 10 dewaxing conditions were: total pressure 40 bar, a hydrogen partial pressure at the reactor outlet of 36 bar, WHSV = 1 kg/l.h, a temperature of 340 °C and a recycle gas rate of 500 Nl/kg feed.

15 The dewaxed oil was distilled, wherein a lighter and a heavier fraction was removed to obtain the final base oil having the improved solvency properties and the properties as listed in Table 2.

Table 2

| | |
|---------------------------------------|---------|
| Density d _{20/4} | 814 |
| Mean boiling point (50 wt% recovered) | 430 °C |
| Kinematic viscosity at 40 °C | 18 cSt |
| Kinematic viscosity at 100 °C | 4.0 cSt |
| Viscosity index | 121 |
| Pour point | -50 °C |
| Noack volatility | 11 wt% |

Example 2

20 Example 1 was repeated except that the dewaxed oil was distilled differently to yield the base oil having the improved solvency properties and other properties as listed in Table 3.

Table 3

| | |
|---------------------------------------|----------|
| Density d _{20/4} | 818 |
| Mean boiling point (50 wt% recovered) | 448 °C |
| Kinematic viscosity at 40 °C | 23.4 cSt |
| Kinematic viscosity at 100 °C | 4.9 cSt |
| Viscosity index | 128 |
| Pour point | -55 °C |
| Noack volatility | 6.8 wt% |

Example 3

74.6 weight parts of a base oil, having the properties as listed in Table 4 and which was obtained by catalytic dewaxing of a hydroisomerised/hydrocracked Fischer-Tropsch product as illustrated by Examples 1 and 2, was blended with 14.6 weight parts of a standard detergent inhibitor additive package, 0.25 weight parts of a corrosion inhibitor and 10.56 weight parts of a viscosity modifier. The properties of the resulting composition are listed in Table 5. Table 5 also shows the 0W-30 specifications for motor gasoline lubricants. It is clear that the composition as obtained in this Example meets the requirements of an 0W30 motor gasoline specification.

Comparative experiment A

54.65 weight parts of a poly-alpha olefin-4 (PAO-4) and 19.94 weight parts of a poly-alpha olefin-5 (PAO-5), having the properties as listed in Table 1 were blended with the same quantity and quality of additives as in Example 3. The properties of the resulting composition are listed in Table 5. This experiment and Example 3 shows that a base oil as obtained by the present invention can be successfully used to formulate 0W-30 motor gasoline lubricants using the same additives as

used to formulate such a grade based on poly-alpha olefins.

Table 4

| | PAO-4 | PAO-5 | Base oil of Example 3 |
|--|---------------|-------|-----------------------|
| kinematic viscosity at 100 °C (1) | 3.934 | 5.149 | 4.234 |
| kinematic viscosity at 40 °C (2) | 17.53 | 24.31 | 19.35 |
| viscosity index (3) | 121 | 148 | 125 |
| VDCCS@ -35 °C (P) (4) | 13.63 | 23.08 | 21.17 |
| VDCCS@ -30 °C (P) (5) | 10.3 | 16 | 14.1 |
| MRV cP @ -40 °C (6) | 2350 | 4070 | 3786 |
| Pour Point °C (7) | less than -66 | -45 | -45 |
| Noack (wt%) (8) | 13.4 | 6.6 | 10.6 |
| Content(**) 1-ring cyclo-paraffins (wt%) | n.a. (*) | n.a. | 13 wt% |
| content 2-ring cyclo-paraffins (wt%) | n.a. | n.a. | 1 wt% |
| Content of 3 and higher ring cyclo-paraffins | n.a. | n.a. | <0.1 wt% |

(*) Not analysed but presumed to be zero due to the manner in which poly-alpha olefins are prepared.

(**) Content as based on the whole base oil composition

5 (1) Kinematic viscosity at 100 °C as determined by ASTM D 445, (2) Kinematic viscosity at 40 °C as determined by ASTM D 445, (3) Viscosity Index as determined by ASTM D 2270, (4) VDCCS@ -35 °C (P) stands for dynamic viscosity at -35 degrees Centigrade and is measured according to ASTM D 5293, (5) VDCCS@ -35 °C (P) stands for dynamic viscosity at -35 degrees Centigrade and is measured according to ASTM D 5293, (6) MRV cP @ -40 °C stands for

10

mini rotary viscometer test and is measured according to ASTM D 4684, (7) pour point according to ASTM D 97, (8) Noack volatility as determined by ASTM D 5800.

Table 5

| | 0W-30 specifi- cations | Example 3 | Comparative experiment A |
|--|------------------------------|-----------|-----------------------------|
| kinematic viscosity at 100 °C (cSt) | 9.3-12.5 | 9.69 | 9.77 |
| VDCCS P @ -35 °C (cP) | 62.0 max | 61.2 | 48.3 |
| MRV cP @ -40 °C (cP) | 60000 max | 17500 | 12900 |
| Yield stress | No | No | No |
| Pour Point (°C) | - | -60 | -60 |
| Noack (wt%) | - | 11.7 | 11.2 |

Example 4-5

5 Base oils as prepared from the same feed as in Examples 1 and 2 under varying conditions were prepared. Properties are listed in Table 6. The cyclo-paraffins and normal and iso-paraffins of the base oil of Example 5 (see Table 6) were further analysed. In Figure 1 the content of the normal and iso-paraffins, 1-ring cyclo-paraffins, 2-ring cyclo-paraffins, etc, in the saturates phase as a function of their respective carbon numbers are shown of this base oil.

10

Table 6

| Base oil type | Example 4 | Example 5 | Base oil as obtained in Example 2 of EP-A-776959 | Base oil as obtained by catalytic dewaxing a Shell MDS Waxy Raffinate over a Pt/synthetic ferrierite catalyst (*) | Base oil as obtained by catalytic dewaxing a Shell MDS Waxy Raffinate over a Pt/synthetic ferrierite catalyst (**) |
|---|-----------|-----------|--|---|--|
| Viscosity Index | 127 | 121 | 151 | 138 | 132 |
| Pour point (°C) | -48 | -54 | -19 | -21 | -39 |
| Kinematic viscosity at 100 °C (cSt) | 4.77 | 4.14 | 4.80 | 4.91 | 4.96 |
| Dynamic viscosity as measured by CCS at -40 °C (cP) | 5500 | 3900 | 6800 | 5300 cP | 5700 cP |

Table 6 (cont'd)

| Base oil type | Example 4 | Example 5 | Base oil as obtained in Example 2 of EP-A-776959 | Base oil as obtained by catalytic dewaxing a Shell MDS Waxy Raffinate over a Pt/synthetic ferrierite catalyst (*) | Base oil as obtained by catalytic dewaxing a Shell MDS Waxy Raffinate over a Pt/synthetic ferrierite catalyst (**) |
|------------------------------|-----------|-----------|--|---|--|
| Saturates content (wt%) | 99.1 | 99.9 | 99.8 | 99.7 | 91.4 |
| Total cyclo-paraffin content | 13.7 | 18.5 | 4.1 | 6.1 | 8.2 |
| 1-ring cyclo-paraffins (wt%) | 11.1 | 16.8 | 3.7 | 4.9 | 6.4 |
| 2-ring cyclo-paraffins | 1.4 | 1.4 | 0.2 | 0.5 | 0.7 |

Table 6 (cont'd)

| Base oil type | Example 4 | Example 5 | Base oil as obtained in Example 2 of EP-A-776959 | Base oil as obtained by catalytic dewaxing a Shell MDS Waxy Raffinate over a Pt/synthetic ferrierite catalyst (*) | Base oil as obtained by catalytic dewaxing a Shell MDS Waxy Raffinate over a Pt/synthetic ferrierite catalyst (**) (1.1) |
|--|-----------|-----------|--|---|--|
| 3 and higher number rings cyclo-paraffins | 1.2 | 0.3 | 0.2 | 0.7 | |

(*) Reaction conditions: total pressure 40 bars, WHSV=1 kg/l/h, gas recycle rate = 700 Nl/kg feed and temperature of 290 °C. (**) as in (*) but at 320 °C dewaxing temperature

C L A I M S

1. Lubricating base oil composition comprising at least 95 wt% saturates, of which saturates fraction between 10 and 40 wt% are cyclo-paraffins and the remainder being n- and iso-paraffins, said composition having a viscosity index of above 120 and a pour point of below -15 °C.
5
8. Base oil according to claim 1, wherein the content of cyclo-paraffins in the saturates fraction is between 10 and 30 wt%.
9. Base oil according to any one of claims 1-2, wherein 10 the content of cyclo-paraffins in the saturates fraction is at least 12 wt%.
10. Base oil according to any one of claims 1-3, wherein the weight ratio of 1-ring cyclo-paraffins relative to cyclo-paraffins having two or more rings is greater than 15 3.
11. Base oil composition according to any one of claims 1-4, wherein the pour point is less than -30 °C, preferably lower than -40 °C.
12. Base oil composition according to any one of 20 claims 1-5, wherein the kinematic viscosity at 100 °C is between 3.5 and 6 cSt and the Noack volatility is between 6 and 14 wt%.
13. Process to prepare a lubricating base oil according to any one of claims 1-6, wherein the following steps are 25 performed:
 - (a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic Fischer-Tropsch product, which product has a 30 weight ratio of compounds having at least 60 or more

carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product of at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms,

5 (b) hydrocracking/hydroisomerising the Fischer-Tropsch product,

(c) separating the product of step (b) into one or more gas oil fractions, a base oil precursor fraction and a higher boiling fraction,

10 (d) performing a pour point reducing step to the base oil precursor fraction obtained in step (c), and

(e) recovering the lubricating base oil from the effluent of step (d).

8. Lubricant formulation comprising the base oil according to any one of claims 1-6 and at least one lubricant additive.

15 9. Formulation according to claim 8, wherein the formulation comprises at most 10 wt% of an additional base oil next to the base oil according to any one of claims 1-6.

20 10. Formulation according to any one of claims 8-9, wherein the formulation has a kinematic viscosity at 100 °C of more than 5.6 cSt, a cold cranking simulated dynamic viscosity at -35 °C according to ASTM D 5293 of less than 62 centiPoise (cP) and a mini rotary viscosity test value of less than 60000 cP according to ASTM D 4684.

30 11. Formulation according to claim 10, wherein the base oil has a pour point of less than -39 °C and a kinematic viscosity at 100 °C of between 3.8 and 5.5 cSt and the lubricant composition has a kinematic viscosity at 100 °C of between 9.3 and 12.5 cSt.

12. Use of a formulation according to any one of claims 9-11 as an 0W-X passenger car motor oil or as an

- 26 -

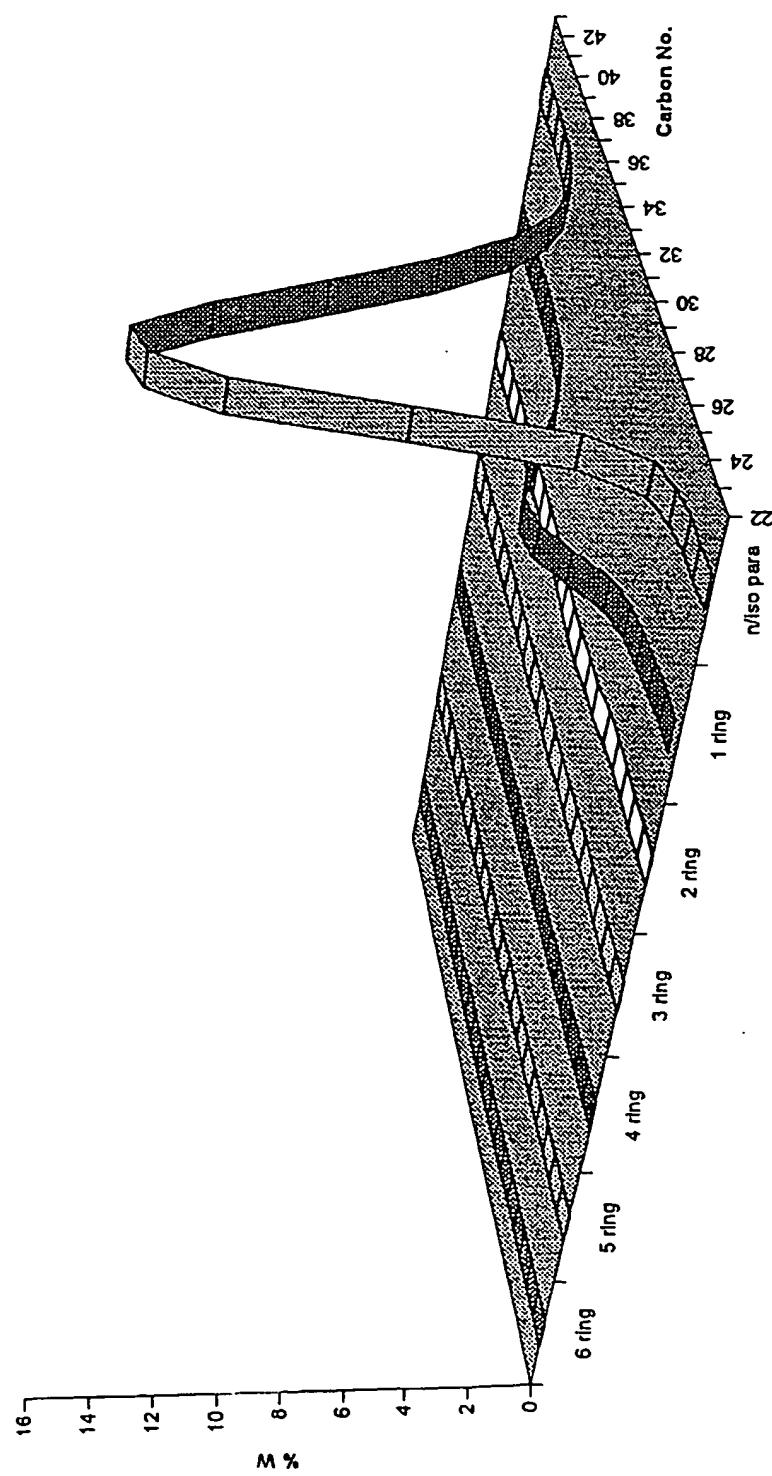
0W-X heavy duty diesel engine oil, where X is 20, 30 or 40.

13. Industrial formulation comprising more than 90 wt% of the base oil according to any one of claims 1-6 and 5 between 0.5 and 3 wt% of an additive.

14. Use of an industrial formulation according to claim 12 as a hydraulic oil or as a turbine oil.

1/1

Fig. 1



(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
22 August 2002 (22.08.2002)

PCT

(10) International Publication Number
WO 02/064710 A3(51) International Patent Classification⁷: C10M 101/02, C10G 2/00, 45/58

(21) International Application Number: PCT/EP02/01634

(22) International Filing Date: 13 February 2002 (13.02.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01301272.9 13 February 2001 (13.02.2001) EP
01400562.3 5 March 2001 (05.03.2001) EP
01402181.0 16 August 2001 (16.08.2001) EP

(71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): DANIEL, Mervyn, Frank [GB/US]; 22111 Vobe Court, Katy, TX 77449 (US). GERMAINE, Gilbert, Robert, Bernard [FR/FR]; Route Departmentale no. 3, F-76650 Petit Couronne (FR). WED-LOCK, David, John [GB/GB]; Pool Lane, Ince, Chester, Cheshire CH2 4NU (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VU, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

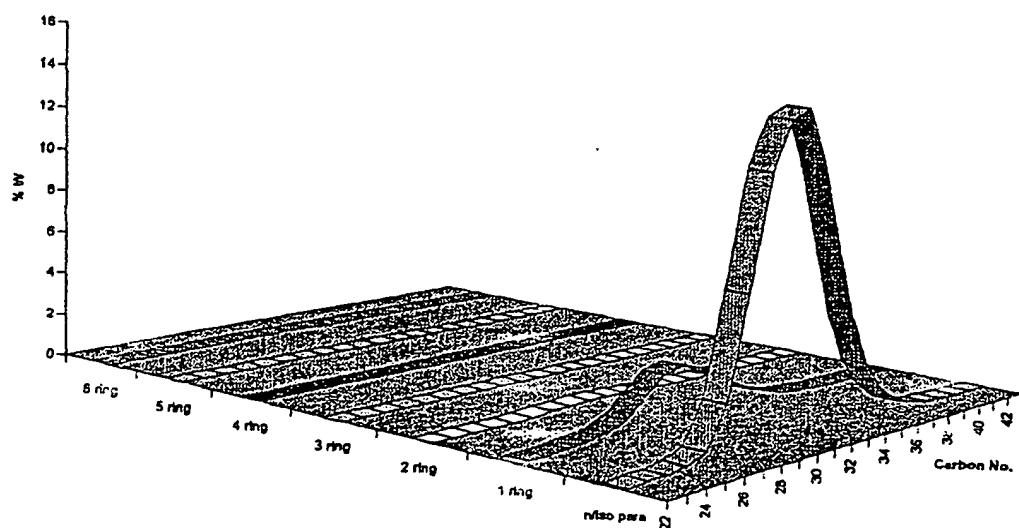
Published:

— with international search report

(88) Date of publication of the international search report:
16 October 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BASE OIL COMPOSITION



WO 02/064710 A3

(57) Abstract: Lubrication base oil composition comprising at least 95 wt % saturates, of which saturates fraction between 19 and 30 wt % are cyclo-paraffins and the remainder being n- and iso-paraffins, said composition having a viscosity index of above 120 and a pour point of below -15 °C.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/01634

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C10M101/02 C10G2/00 C10G45/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C10M C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | EP 0 435 670 A (NIPPON OIL CO LTD) 3 July 1991 (1991-07-03) claims 1,3-8,10 page 6, line 27 table 2 | 1,6, 12-14 |
| A | WO 00 71646 A (LUBRIZOL CORP) 30 November 2000 (2000-11-30) claims 20-23,25 page 4, line 25 - line 28 | 1 |
| A | WO 00 15736 A (EXXON RESEARCH ENGINEERING CO) 23 March 2000 (2000-03-23) claims 1,6,8-11 | 1,7-9, 12-14 |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

| | |
|--|--|
| Date of the actual completion of the international search | Date of mailing of the international search report |
| 22 July 2002 | 29/07/2002 |
| Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Authorized officer De Herdt, O |

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/01634

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | US 6 165 949 A (HABEEB JACOB J ET AL) 26 December 2000 (2000-12-26) claims 1,4,5,7,17,25,27,28 column 9, line 24-26 — | 1,7-9, 12-14 |
| A | WO 99 20720 A (MOBIL OIL CORP) 29 April 1999 (1999-04-29) cited in the application the whole document — | 10-12 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/01634

| Patent document cited in search report | | Publication date | | Patent family member(s) | Publication date |
|--|---|------------------|--|---|--|
| EP 0435670 | A | 03-07-1991 | | JP 2724508 B2 JP 4036391 A JP 2724510 B2 JP 4068082 A JP 2724512 B2 JP 4120193 A JP 2938487 B2 JP 3223393 A DE 69011829 D1 DE 69011829 T2 EP 0435670 A1 US 5372703 A | 09-03-1998 06-02-1992 09-03-1998 03-03-1992 09-03-1998 21-04-1992 23-08-1999 02-10-1991 29-09-1994 13-04-1995 03-07-1991 13-12-1994 |
| WO 0071646 | A | 30-11-2000 | | AU 5288600 A EP 1200540 A1 WO 0071646 A1 | 12-12-2000 02-05-2002 30-11-2000 |
| WO 0015736 | A | 23-03-2000 | | US 6332974 B1 AU 5680899 A BR 9913583 A EP 1144551 A2 NO 20011245 A WO 0015736 A2 | 25-12-2001 03-04-2000 22-05-2001 17-10-2001 10-05-2001 23-03-2000 |
| US 6165949 | A | 26-12-2000 | | AU 5690299 A BR 9913410 A EP 1114132 A2 NO 20011123 A US 2002086803 A1 WO 0014188 A2 | 27-03-2000 22-05-2001 11-07-2001 02-05-2001 04-07-2002 16-03-2000 |
| WO 9920720 | A | 29-04-1999 | | AU 739549 B2 AU 1088699 A BG 104433 A BR 9813120 A CA 2306886 A1 CN 1279708 T EP 1029029 A1 HR 20000259 A1 HU 0100005 A2 JP 2001520302 T NO 20002010 A PL 340097 A1 SI 20333 A SK 5802000 A3 TR 200001084 T2 WO 9920720 A1 US 6090989 A ZA 9809526 A | 18-10-2001 10-05-1999 31-01-2001 15-08-2000 29-04-1999 10-01-2001 23-08-2000 31-12-2000 28-05-2001 30-10-2001 14-06-2000 15-01-2001 28-02-2001 11-06-2001 21-09-2000 29-04-1999 18-07-2000 19-04-2000 |